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Anti-Stokes luminescence in Pr^{3+} activated crystalline ZBLAN (Zr, Ba, La, Al & Na) fluoride phosphor

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Abstract : Infrared-to-visible up-conversion in Pr^{3+} activated ZBLAN fluoride crystalline phosphors has been investigated at room temperature for different activator concentrations. In the excitation spectra as well as in the emission spectra, initially the intensity increases with activator concentration, attains an optimum value and then it decreases with further increase in the activator concentration. It seems that blue excitation of the phosphor is due to Excited State Absorption (ESA) mechanism. The 2nd power dependence of the blue fluorescence from the $^3P_0$ state under IR pumping of $^1G_4$ state indicates a dominant two photon ESA mechanism. The mechanism of anti-Stokes luminescence in an unique optical activator Pr^{3+} in the ZBLAN fluoride host material, is discussed.

Keywords : Anti-Stokes luminescence, up-conversion, ZBLAN

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1. Introduction

When photoluminescence is observed for energies larger than the excitation energy, such phenomenon is known as anti-Stokes luminescence. The study of anti-Stokes luminescence due to excitation energy accumulation by RE^{3+} ions is based on the work of Bloembergen [1], Ovsyankin and Foefilov [2], Foefilov [3] and Auzel [4] where various mechanisms have been proposed for accumulation of luminescence energy by ions : (i) stepwise (successive) absorption of IR quanta by the same radiative ion, (ii) co-operative (simultaneous) sensitization of a radiative ion by two or more excited ions, and (iii) stepwise (successive) sensitization of a radiative ion by other excited ions.

Although all these mechanisms can occur in various solid materials with RE^{3+} ions, the study of up-conversion in Pr^{3+}-doped ZBLAN (Zr, Ba, La, Al & Na) fluoride glasses points out different up-conversion mechanisms namely, exited state absorption (ESA) and energy transfer up-conversion (ETU) mechanisms [5].

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The interaction of trivalent ions of rare earth elements (RE^{3+}) in excitation state has been analyzed to a considerable degree with the use of kinetic methods to investigate the excitation energy transformation in condensed media [2,3,6,7]. To distinguish between the mechanisms of interaction between the impurity system and the anti-Stokes radiation, many criteria are subsequently developed, which are based on an analysis of the optical spectra and of the dependence on the intensity particle concentration and on the excitation density [3,6,8]. It is reliably established that in most cases, the process of population of highly excited states of RE^{3+} ions in condensed media is collective and proceeds *via* many stages.

The branched structure of the states of the RE^{3+} ions, in conjunction with multistage character of the process, leads to an extraordinary variety of mechanisms, whereby the highly excited states of those ions are populated. In many cases, it remained unclear which of the RE^{3+} ion levels are participating in the population of the highly

excited states, from which the anti-Stokes radiation is observed, and which stages of the non-radiative energy transfer limit the process of population of those states in each concrete case. These questions are closely related to more general unsolved problem of the influence of the crystalline host on the effectiveness of the anti-Stokes energy conversion in systems, with rare earth activators. It is well known that by the virtue of the good screening of the $4f$ electrons, the multiple energies and Einstein coefficient of the intermultiplet transition of the RE^{3+} ions, vary little on going from one matrix to another. It is also known, however, that in various hosts, for the same interactions of the RE^{3+} ion pair, different excited states are populated with different effectiveness [9–11]. The crystal lattice determines the probability of the electron-phonon interaction and the Stark structure of the multiplets. This in turn, can strongly influence each stage of the successive energy transfers.

Among a variety of hosts for rare earth ions, the heavy metal fluoride materials are very much preferred hosts, as they present a high transparency from UV to IR region. Besides, most importantly due to their low multiphonon emission rates, rare earth-doped fluoride materials exhibit large up-conversion efficiencies.

As an activator, the trivalent praseodymium ion is an interesting optical activator, since its energy level spectrum contains several metastable multiplets $^1G_4$ $^1D_2$ $^3P_{0,1,2}$ that offer the possibility of simultaneous emission in the blue, green, orange, red and infrared. Furthermore, the broadband inter configuration $4f^2 \rightarrow 4f, 5d$ transitions of Pr^{3+} which are used in scintillator detectors of ionizing radiation [12,13], offer the potential for tunable laser action at near UV wavelengths. While most up-conversion studies in Pr^{3+}-doped materials have focused $^1D_2 \rightarrow {}^3P_0$ processes [14,15], the alternate $^1G_4 \rightarrow {}^1D_2 \rightarrow {}^3P_0$ process was only observed in Pr^{3+} fibers [16,17] and has not been well characterized.

The present paper reports the spectroscopy of anti-Stokes luminescence of Pr^{3+}-doped ZBLAN fluoride crystalline phosphor, where the phosphor was excited by IR radiation. In the present investigation, major emphasis has been given to understand the effect of activator (Pr^{3+}) concentration on the IR to visible conversion process, and also to understand the mechanism of this up-conversion.

2. Experimental

2.1. Phosphor preparation :

The solid state diffusion technique was utilized for preparing Pr^{3+}-activated ZBLAN fluoride phosphor. For preparation, the molar compositions used were 53% ZrF_4, 20% BaF_2, 4% LaF_3, 3% AlF_3 and 20% NaF (hence, acronym ZBLAN). Samples of different praseodymium concentrations were prepared from batches containing 0.02%, 0.05%, 0.1%, 0.15%, 0.3% and 1% in weight of PrF_3 (*i.e.*, 200, 500, 1000, 1500, 3000 and 10000 ppm Wt of Pr^{3+} ions). The entire constituents were taken in stoichiometric proportions and placed in Pt crucible. The crucible was gradually heated up to 1000°C by placing it in the furnace and kept at this temperature for two hours, and then cooled slowly to room temperature. Thus, Pr^{3+}-doped ZBLAN fluoride phosphors with various activator concentrations were obtained in powder form.

2.2. Optical measurement :

The experimental setup used for recording the anti-Stokes luminescence emission intensity and excitation spectra is shown in Figure 1. The main constituents of the setup are grating monochromator, light source (250 W IR lamp), constant deviation spectrometer and detector unit. The detector unit consists of high voltage power supply (EHT-extra high tension), photomultiplier tube (PMT), and a digital picometer.

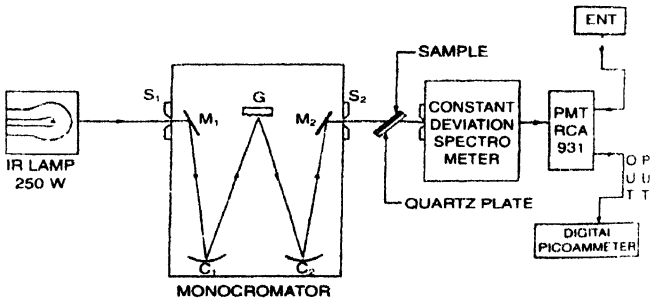

Figure 1. Experimental setup for the measurement of anti-Stokes luminescence and dependence of IR emission intensity on excitation intensity

2.2.1. Measurement of infrared excitation spectra :

For the measurement of anti-Stoke luminescence excitation characteristics, the phosphor was excited by the light from 250 W IR lamp. Passing through the entrance slit of grating monochromator, it was allowed to fall on the phosphors. The light emitted from the phosphors was allowed to fall on to the entrance slit of constant deviation spectrometer, output of which was fed to a photomultiplier tube having a narrow slit in its housing. The light from the spectrometer was detected by an RCA 931 photomultiplier tube (PMT), which was operated at 750 volts fed by high voltage power supply. The output of the PMT was fed to a digital picoammeter. Thus, by

measuring the emission at a fixed wavelength (480 nm) and by rotating the drum of monochromator, the relative intensities for different wavelengths were measured, which in turn, provided the infrared excitation spectra.

2.2.2. Measurement of infrared emission spectra :

For the emission spectra, the drum of grating monochromator was fixed at 919 nm, while the drum of constant deviation spectrometer was varied from 420 nm to 560 nm. Similar procedure as above, is followed and by rotating the drum of the constant deviation, intensities for different wavelengths were measured, which in turn, provided the IR emission spectra.

2.2.3. Measurement of dependence of IR emission intensity on the excitation intensity :

The experimental setup shown in Figure 1 with minor additions to it, is used for recording the output intensity. The detector unit now consists of a photodetector along with a multimeter in addition to above units.

The photodetector was placed on the exit slit of grating monochromater. The output of photodetector was given to multimeter and hence, the source intensity was measured. To change the source intensity, the distance of IR source from the grating monochromater was changed. In order to measure the sample intensity, first of all we measured the source intensity and then, we removed photodetector from the exit slit of grating monochromater. In the present experiment, the Pr^{3+}-doped ZBLAN fluoride phosphor with 500 ppm wt activator concentration was excited by IR lights of various intensities (using IR lamp) passing through an entrance slit of the monochromator. The light emitted from the phosphor falls onto the entrance slit of the constant deviation spectrometer.

For the measurements, the drum of monochromator was fixed at 919 nm and that of constant deviation spectrometer was fixed at 480 nm and then by changing the distance of source from monochromator, we measured emission intensities for various input excitation intensities.

3. Results

Figure 2 shows the IR excitation spectra of ZBLAN fluoride phosphor doped with Pr^{3+}. The measurements were done at room temperature. In this case, the samples with 200, 500, 1500, 3000 and 10000 ppm wt concentrations of Pr^{3+} ions were taken. The phosphor was excited by light having wavelength in the range of 780 nm to 940 nm and emission was measured at

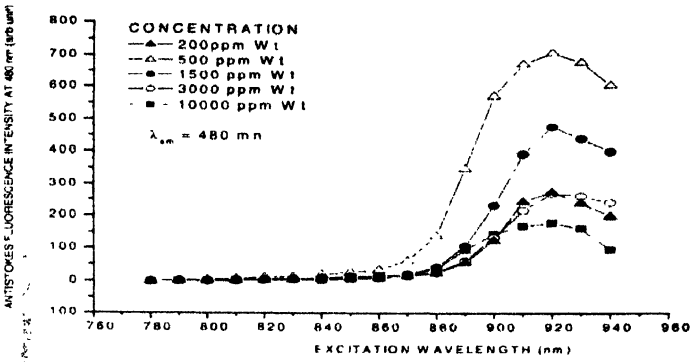

Figure 2. Excitation spectra of the blue up-conversion fluorescence (480 nm) of Pr^{3+}-doped ZBLAN fluoride phosphors at room temperature (concentrations of 200, 500, 1500, 3000 and 10000 ppm wt of Pr^{3+} were taken).

480 nm. It is seen that initially emission intensity is constant and low with the increase in the excitation wavelength, and only after 860 nm excitation wavelength, it increases with the increase in excitation wavelength, attains an optimum value for 919 nm and then decreases with further increase in the wavelength. Also it is evident from the figure that initially with the increase in concentration of Pr^{3+}, the intensity increases, attains optimum value for 500 ppm wt concentration of Pr^{3+} and then decreases.

Figure 3 shows the IR emission spectra of ZBLAN fluoride phosphor doped with Pr^{3+} ions. The measurement of visible emission intensity as a function of Pr^{3+} concentration was done at room temperature. In this case, the samples with 200, 500, 1500, 3000 and 10000 ppm wt concentration of Pr^{3+} ions were taken. The phosphor was excited by light having wavelength of 919

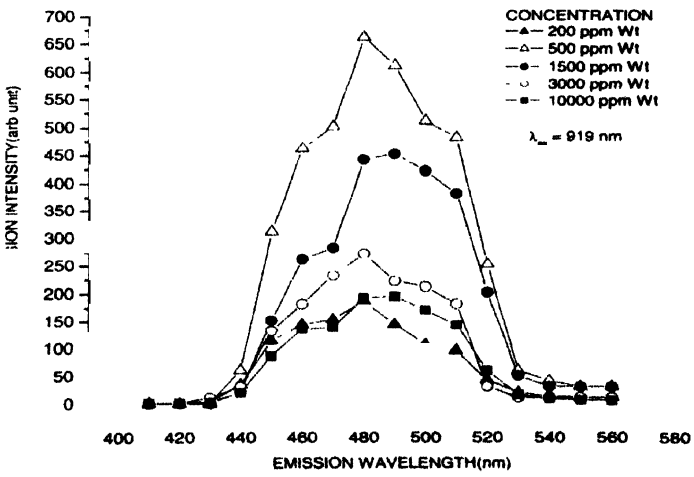

Figure 3. Up-converted visible fluorescence spectra of Pr^{3+}-doped ZBLAN fluoride phosphor for infrared excitation of 919 nm at room temperature (Pr^{3+} concentrations of 200, 500, 1500, 3000 and 10000 ppm wt were taken).

nm and emission was measured from 420 nm to 560 nm. Effective peck of high intensity was found at 480 nm for different concentration of activator (Pr^{3+}). It is to be noted that initially the intensity increases with activator concentration, attains an optimum value for 500 ppm wt concentration of Pr^{3+} and then it decreases with further increase in the activator (Pr^{3+}) concentration.

Figure 2 also shows the activator (Pr^{3+}) concentration dependence of IR excitation spectra of ZBLAN fluoride phosphor doped with Pr^{3}. It is found that in IR excitation spectra initially the emission intensity increases with increasing concentration of Pr^{3+}, attains an optimum value for 500 ppm wt concentration of Pr^{3+} and then decreases with further increase in the concentration of the activator.

Figure 3 also illustrates the activator concentration dependence of the IR emission spectra of ZBLAN fluoride phosphor doped with Pr^{3+}. It is found that in IR emission spectra, initially the emission intensity increases with increasing concentration of Pr^{3+}, attains an optimum value for 500 ppm wt concentration of Pr^{3+}, then decreases with further increase in the concentration of the activator.

Figure 4 shows the dependence of anti-Stokes luminescence on the intensity of IR exciting light source for Pr^{3+}-doped ZBLAN fluoride phosphor. In this case, the wavelength of excitation light was kept at 919 nm and that of emission was kept at 480 nm (where emission peak of IR emission spectrum was found). It is evident from the figure that emission intensity increases with the increase of excitation intensity. The slope of the line is found to be two, for the blue emission.

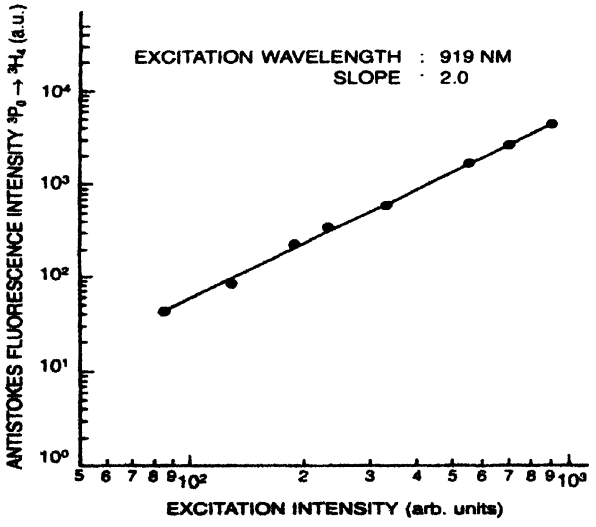

Figure 4. Intensity dependence of the blue up-conversion fluorescence (480 nm) with IR excitation at 919 nm for Pr^{3+}-doped ZBLAN fluoride phosphor.

4. Discussion

4.1. Mechanism for anti-Stokes luminescence in Pr^{3+}-doped ZBLAN fluoride phosphor :

In our work, the emission and excitation spectra, we have obtained for ZBLAN fluoride phosphor activated by Pr^{3+}, can be explained by sequential two photon absorption.

Two photon up-conversion processes can by divided in two main classes, which refer to population effects in a real intermediate metastable level or to nonlinear effects. In the latter case, second harmonic generation, two photon absorption, or parametric oscillation are examples, while the former case gathers excited state absorption (ESA) as well as summation of photons by energy transfer up-conversion (ETU), cooperative sensitization or cooperative luminescence with a lot of illustration in rare earth-doped materials [18, 19]. Among these mechanisms, ESA and ETU are the most efficient. Indeed the ESA process fills instantaneously the upper excited state, even if one of the step involved in the process is off-resonance, and the decay of the up-converted fluorescence is identical to the decay following direct one photon excitation. On the other hand, the ETU process, fills the upper excited state after a rise time, which depends on the energy transfer between the ions [5].

The emission and excitation spectra of Pr^{3+}-doped ZBLAN fluoride phosphors are in agreement with the ESA mechanism dominantly. Figure 5 shows energy level diagram of Pr^{3+} ions in ZBLAN material. Figure shows

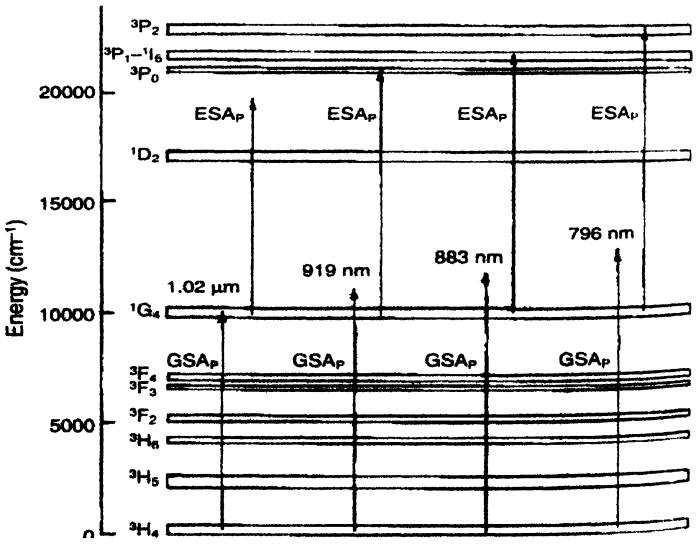

Figure 5. Energy level diagram of Pr^{3+} ions in ZBLAN material. Positions and broadenings have been deduced from absorption and luminescence measurement under near IR pumping, blue fluorescence is maximum at four wavelengths : 1.02 μm, 919, 883 and 796 nm.

that blue fluorescence is possible at four wavelengths : 1.02 μm, 919, 883 and 796 nm. The maximum blue output emission is found at excitation wavelength of 919 nm, which corresponds to the ESA (Excited State Absorption) transition $^1G_4 \rightarrow {}^3P_0$. The only possible (ESA) mechanism resulting in the excitation of the $^3P_0$ state with IR photons should come from the excited $^1G_4$ state. In that case, the IR pump wavelength must be resonant only with the absorption from the intermediate metastable $^1G_4$ state to $^3P_0$ state, but not with the absorption from the ground $^3H_4$ state [18]. Thus, the first photon is nonresonantly absorbed in a weak phonon band associated with $^3H_4 \rightarrow {}^1G_4$ transition.

It is evident from the above discussion that the blue fluorescence of $^3P_0$ level can be attributed to two regimes of up-conversion mechanisms depending upon the fact that the single excitation wavelength is in resonance with a ground state absorption or with an excited state absorption.

The resonant ESA case is in agreement with the established fact that ESA is the main mechanism to achieve IR to blue up-conversion in Pr^{3+}-doped crystalline materials [18]. Thus all the spectra can be readily assigned to ESA transition of ($^1G_4 \rightarrow {}^3P_0$) or we can say two-step ESA transition of ($^3H_4 \rightarrow {}^1G_4 + {}^1G_4 \rightarrow {}^3P_0$).

4.2. Dependence of anti-Stokes luminescence intensity on the concentration of activator :

As the concentration of dopant increases, initially the number of luminescence centers increases and it causes the increase in the anti-Stokes luminescence intensity. For higher values of concentration of dopant, concentration quenching of luminescence intensity takes place and therefore, the anti-Stokes luminescence intensity decreases for higher concentration of dopant in ZBLAN fluoride phosphor. Thus the anti-Stokes luminescence intensity is optimum for a particular concentration of the activator.

4.3. Excitation intensity dependence of anti-Stokes luminescence in Pr^{3+}-doped ZBLAN fluoride phosphor :

The number of IR photons absorbed per photon emitted for an up-conversion mechanism can be identified from the dependence of the emission intensity on infrared input intensity.

The visible output intensity (I_V) of the sample will be proportional to a power n of the infrared excitation intensity (I_{IR}) *i.e.*,

$$(I_V) \propto (I_{IR})^n,$$

where n is the number of infrared photons absorbed per visible photon emitted. Figure 4 shows a plot of logarithm of I_V *versus* the logarithm of I_{IR} for the blue emission band. The data have been fitted to straight line in the plot, the slope of which is equal to two (= n). Since the slope is two, a quadratic behavior of the blue fluorescence intensity *versus* pumping excitation intensity is established. This agrees very well with a two-photon process, which corresponds to the ESA transition of $^3H_4 \rightarrow {}^1G_4 + {}^1G_4 \rightarrow {}^3P_0$.

5. Conclusions

The main conclusions drawn from the studies of spectroscopy of the anti-Stokes luminescence of Pr^{3+}-doped ZBLAN fluoride phosphors are as follows :

(i) In IR emission spectra of Pr^{3+}-doped ZBLAN fluoride phosphor, one effective peak of high intensity is found in blue region of visible spectrum while the samples were excited by 919 nm.

(ii) In IR excitation spectra of the phosphor, initially the emission intensity is low and constant up to a certain wavelength and then it increases with increase in wavelength, attains an optimum value for 919 nm and then decreases with further increase in wavelength.

(iii) Both, in the emission spectra and in the excitation spectra, initially the anti-Stokes luminescence intensity increases with activator concentration, attains an optimum value and then decreases with further increase in the activator concentration.

(iv) The up-conversion of Pr^{3+}-doped ZBLAN fluoride phosphor is attributed to two-photon absorption process for blue (480 nm) emission band. The dominant mechanism is a nonresonant two-step ESA transition of ($^3H_4 \rightarrow {}^1G_4 + {}^1G_4 \rightarrow {}^3P_0$).

(v) The plot of the logarithm of intensity of blue (480 nm) up-conversion emission *versus* the logarithm of excitation intensity for 919 nm light is found to be straight line with a slope of two. This indicates that two photon absorption is taking place to populate $^3P_0$ level of Pr^{3+}.

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